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Energy Procedia 119 (2017) 845–851

Energy Procedia

www.elsevier.com/locate/procedia

International Conference on Technologies and Materials for Renewable Energy, Environment and Sustainability, TMREES17, 21-24 April 2017, Beirut Lebanon

Effect of *lecaniodiscus cupaniodes* extract in corrosion inhibition of normalized and annealed mild steels in 0.5 M HCl

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Abstract

The effect of Lecaniodiscus cupaniodes extract as a green inhibitor on the degradation behaviour of normalized and annealed mild steels in 0.5 M hydrochloric acid (HCL) was evaluated. Gravimetric and potential measurements were used for the experimental work. The results revealed that Lecaniodiscus cupaniodes performed effectively at inhibiting the rate of corrosion attack on the heat-treated steels in 0.5 M HCl medium with an average inhibition efficiency of 90 percent (%). However, the effectiveness of the extract as an inhibitor was found to be dependent on the exposure period for the annealed samples. Corrosion rates of the two heat-treated steels were significantly affected by the concentration of lecaniodiscus cupaniodes extract. At the end of the 34-days exposure period, only 5 ml concentration of the extract gave the best inhibition efficiency for the annealed and normalized steels - 77.09 % and 82.57 % respectively. The significance of the results was further determined via two-factor Analysis of Variance (ANOVA) test. The statistical analysis confirms the effect of extract concentration and exposure time on corrosion behaviour with 95 percent confidence.

Peer-review under responsibility of the Euro-Mediterranean Institute for Sustainable Development (EUMISD).

Keywords: heat treatment; corrosion; inhibitor; ANOVA; steels; *lecaniodiscus cupaniodes*

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10.1016/j.egypro.2017.07.136

1. Introduction

Mild steel, being the most important engineering and construction material; accounts for approximately 80 % of all metals produced. All segments of the energy sector, including nuclear, wind power, electric and natural gas, demand mild steel for infrastructure. This degree of prominence is attained by the steel because it combines strength, ease of fabricability into many shapes, and a wide range of properties along with low cost. Likewise, it is possible to give a wide range of mechanical properties to mild steels by changing the size and shape of the grains through heat treatment [1]. However, the electrical, corrosion and thermal conductivity of mild steels are slightly altered during heat treatment process. These trends have led to demand for steel of greater strength, improved corrosion resistance as well as ductility.

With the world going green, the exploration of natural plants as corrosion inhibitors for metals is becoming the subject of various research work [2-5] due principally to the low cost and eco-friendliness of these products, and is fast replacing the synthetic and expensive organic inhibitors. Plant extracts constitute several organic compounds which have corrosion inhibiting capacities. The yield of these compounds as well as the corrosion inhibition abilities vary widely depending on the part of the plant [6].

Lecaniodiscus cupaniodes is a plant specie of the family *Sapindaceae*. It is a tropical plant widely distributed in Africa and Asia [7,8]. A study by [8] reveals that *lecaniodiscus cupaniodes* contains 2.37% alkaloids, 0.336% saponnin, 0.012% tannin, 0.008% phenol and 0.002% anthraquinone. *Lecaniodiscus cupaniodes* has been proved to be a potent malaria inhibiting agent. However, its potential for inhibiting corrosion in metallic structures has not been exploited. Therefore, this study is aimed at determining the optimal inhibition efficiency attainable with leave extracts of *lecaniodiscus cupaniodes* plant on heat-treated mild steel in 0.5 M HCl.

2. Experimental

2.1. Materials and test environments

Test coupons were machined from new mild steel rods, obtained from the commercial market in Lagos, Nigeria. The determined chemical composition of the steel includes: 0.140 C, 0.097 Si, 0.576 Mn, 0.115 Ni, 0.075 Cr, 0.015 Mo, 0.002 V, 0.285 Cu, 0.015 Sn, 0.007 Co, 0.005 W, 0.032 S and the balance Fe (Wt. %). The machined samples with dimensions, 2 cm × 0.5 cm were subjected to annealing and normalizing heat treatments by heating the specimens in a muffle furnace up to 850ºC, and soaking for 50 minutes. To achieve the annealed and normalized states, the heated samples were furnace-cooled and air-cooled respectively. Afterwards, the samples were degreased in ethanol and allowed to dry.

0.5 M dilute HCl was prepared as the test environment using analar grade reagents and ultra-pure water.

2.2. Preparation of plant extract

The leaves of *lecaniodiscus cupaniodes* were air dried for a period of 21 days and ground into powder weighing about 4kg in all. The extracts were removed by soaking the dried leaves in ethanol for a period of five days and filtering afterwards. The resulting extract solution was left for about 60 hours after which the remaining ethanol evaporated. A variation of 1 - 5ml of the extract concentration was used for the corrosion tests.

2.3. Mass loss tests and Potential Measurements

For immersion tests, the heat-treated mild steel samples were dry-abraded with emery paper grades of 60, 180, 320 and 600 microns. The samples were cleaned with acetone and initial weight was measured and recorded. The corrosion media was poured into small plastic bowls of about 500ml in which the heat-treated mild steel specimens were suspended. Weight measurements were taken at two-day intervals for a total period of 34 days.

For potential measurements, flexible copper wire of about 15 cm was joined by soldering to one surface of each steel specimens and inserted into cylindrical-shaped araldite mold with the use of beverage cocks. They were allowed to dry for 24 hours, thereafter the base was removed to reveal only an exposed area of the metal sample which was tested in the corrosion media. Initial potential readings were taken and further subsequent readings were also taken at two-days interval for a period of 34 days. A digital voltmeter and saturated calomel electrode (SCE) were used to take the potential measurements. All the experiments were performed at ambient temperature of 27°C.

2.4. Determination of corrosion rates and inhibitor efficiency

Corrosion rate in millimeter per year (mm/yr.) was determined for normalized mild steel in each test condition using the procedure described in ASTM Standard G1-03 [9]. The equation is given as

$$C.R. = K \times W / A \times T \times D \quad (1)$$

Where $C.R.$ = corrosion rate in mm/yr.
K = 8.76 x 10^4, a constant
W = mass loss in g
A = sample area in cm^2
D = density in g/cm^3
T = exposure time in hours.

The inhibitor efficiency (*I.E.* in percentage) was calculated using equation (2) given as

$$I.E. = \frac{CR_{uninhibited} - CR_{inhibited}}{CR_{uninhibited}} \times 100 \quad (2)$$

3. Results and Discussion

3.1. Influence of Lecaniodiscus cupaniodes extract on mass loss-corrosion rates

Figure 1 shows the variation of corrosion rate with exposure time obtained for annealed and normalized mild steels without inhibitor. Mild steel in the annealed condition exhibited higher corrosion rates in 0.5 M HCl in comparison to the normalized steel. However, similar trend was observed in the corrosion rates of both samples as exposure time increased.

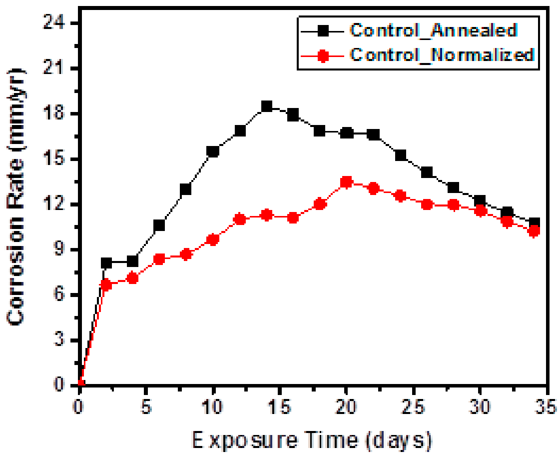

Figure 1: Variation of corrosion rate with exposure time for heat-treated mild steel (control tests).

For the annealed condition, corrosion rates increased with increase in exposure time up to 18.5151 mm/yr. at 14 days, followed by a gradual decrease in corrosion rate until the end of the experiment. Similarly, the normalized condition revealed increase in corrosion rate up to 13.4915 mm/yr. at 20 days, followed by the decreasing trend. The latter decrease in corrosion rate with increase in exposure time suggests passivation action of the oxide films with prolonged exposure to the environment.

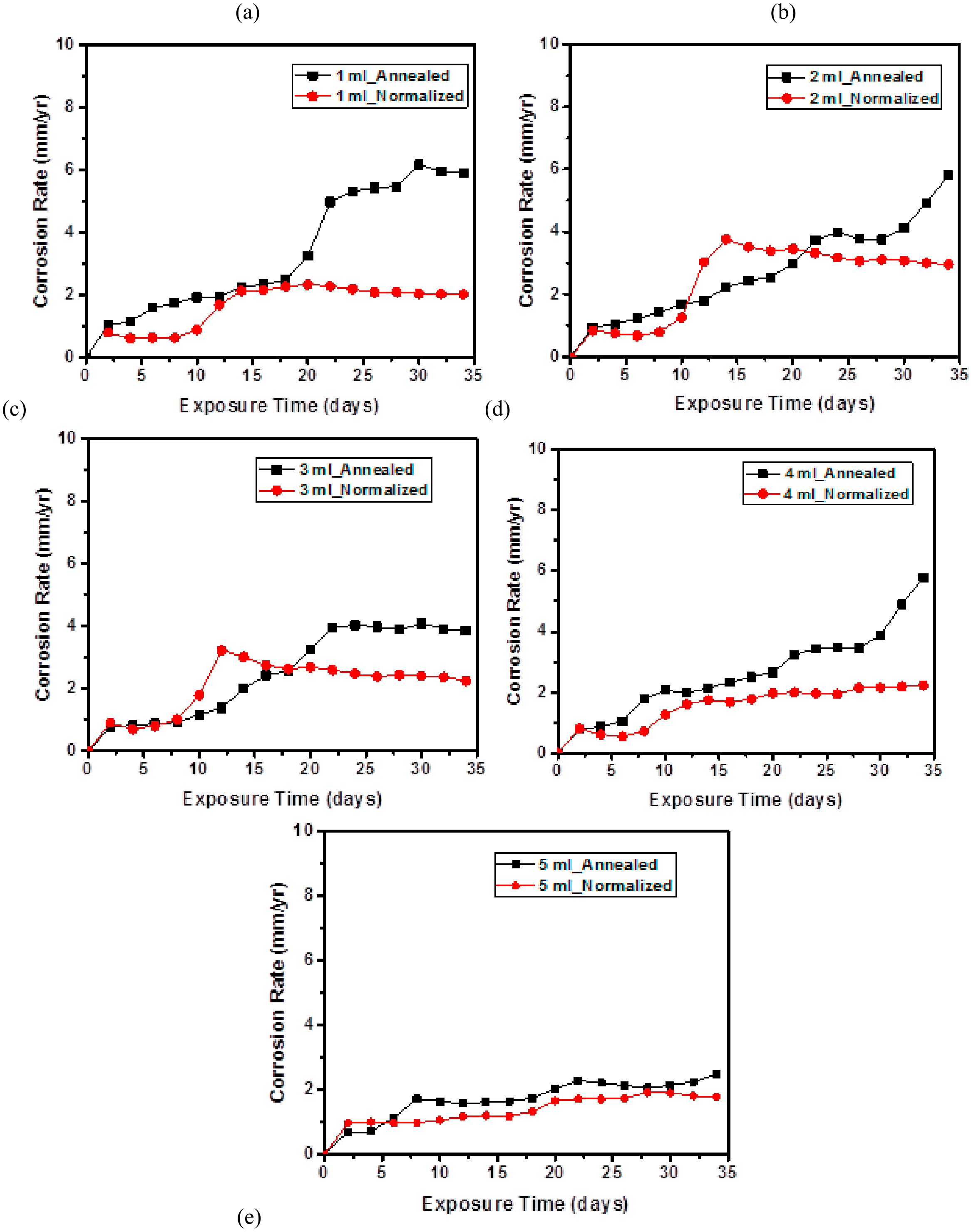

Figure 2: Variation of corrosion rate with exposure time for heat-treated mild steel in the presence of 1-5 ml (a-e) lecaniodiscus cupaniodes extract.

Figures 2a-2e shows the variation of corrosion rates for both annealed and normalized steels in 0.5 M HCl and in the presence of 1-5 ml *lecaniodiscus cupaniodes*. The corrosion rates are seen to be generally low (0-6 mm/yr.) due to the inhibiting effect of the plant extract. The chemical constituents of *lecaniodiscus cupaniodes*, particularly tannin and saponnin have the aptitude of displaying the electrochemical activity of robust adsorption to the steel surface, thereby slowing down the anodic dissolution of the metal in the corrosive environment. It must be pointed out that the response of the annealed samples to exposure time in the presence of the inhibiting plant extract differs from the trend displayed by the normalized samples. Corrosion rate of annealed samples increased with exposure time while that of the normalized samples decreased. This signifies that there is a significant effect of exposure time on the degradation behaviour of annealed mild steel samples in the test environment when *lecaniodiscus cupaniodes* is present. The potency of the extract reduces as exposure time increases. On the other hand, for normalized mild steel, the protective and adsorbent action of the extract increases with increase in exposure time, resulting in reduced corrosion rate.

The significance of the effects of lecaniodiscus cupaniodes extract and exposure time on the corrosion rates obtained in this study was determined by two-factor analysis of variance (ANOVA) test. The separate and combined effects of these variables was determined as well as the total variation within each sample relative to the total variation between the samples following the procedure reported in [10]. Tables 1 and 2 show the ANOVA results obtained for annealed and normalized steel conditions after the statistical tests.

Table 1. ANOVA analysis for annealed mild steel showing the influence of exposure time and extract concentration

Source of Variation	**SS**	**DF**	**MS**	**F**	**Significance F (95% confidence)**
Exposure Time	342.71	17	20.16	10.10	1.75
Concentration of LC	1749.27	5	349.85	175.37	2.33
Residual	169.57	85	1.99		
Total	2261.55	107			

Table 2. ANOVA results for normalized mild steel showing the influence of exposure time and extract concentration

Source of Variation	**SS**	**DF**	**MS**	**F**	**Significance F (95% confidence)**
Exposure Time	42805.32	17	2517.96	0.29	1.75
Concentration of LC	690563.44	5	138112.69	16.04	2.33
Residual	732081.81	85	8612.73		
Total	1286.95	107			

From the ANOVA test results shown in Table 1, it can be confirmed with 95 % confidence, that exposure period and *lecaniodiscus cupaniodes* extract concentration significantly affects the corrosion rate of annealed mild steel in 0.5 M HCl. While exposure time had no significant effect on corrosion rate of normalized steel, the concentration of *lecaniodiscus cupaniodes* has a significant effect as confirmed from the ANOVA test with 95 % confidence.

3.2. Inhibition Efficiency

Figure 3 shows the variation of inhibition efficiency of *lecaniodiscus cupaniodes* extract on (a) annealed and (b) normalized steel samples in 0.5 M HCl. For the annealed samples, highest inhibition efficiency values were obtained in the exposure range of 0-15 days. Afterwards, there was a decreasing trend in efficiency of *lecaniodiscus cupaniodes* extract in inhibition as the exposure period increased. A similar decreasing trend was observed for the normalized steel from 10 days of exposure. The decreasing trend was exhibited by all the extract concentrations (1-5 ml). At the end of 34 days' exposure period, 5 ml concentration gave the highest inhibition efficiency of 77.09 % and 82.57 % for the annealed and normalized steels respectively. However, a high inhibition efficiency value of 93.46 % was achieved with 4 ml of the extract within 6 days on the normalized steel. Since this was the case, it must be stated that there is a relapse in the potency of *lecaniodiscus cupaniodes* absorbent species on passivation of the steel with increase in exposure time.

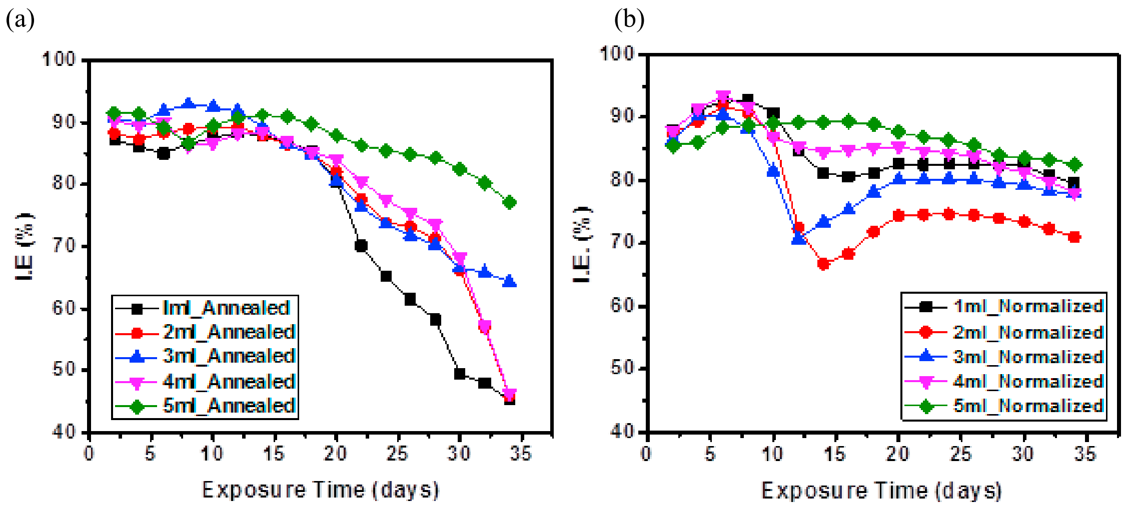

Figure 3: Variation of inhibition efficiency with exposure time for heat-treated mild steel in the presence of 1-5 ml lecaniodiscus cupaniodes extract for (a) annealed and (b) normalized mild steels.

The annealed steel was likewise inhibited with a highest extract efficiency of 92.93 % at 8 days. Furthermore, it is interesting to note that greater protection was achieved for the normalized steels, which compares well with the corrosion rate results where least corrosion rate values were recorded for the same steel. This is due to the protective action of the adsorbent species from the plant extract, on the surface of the steel samples.

3.3. Effect of Lecaniodiscus cupaniodes extract on Potential Measurements

Potential measurements were taken for the heat-treated steel samples over a period of 34 days at 2-days interval. Figure 4 shows the variation of the potential readings with exposure time.

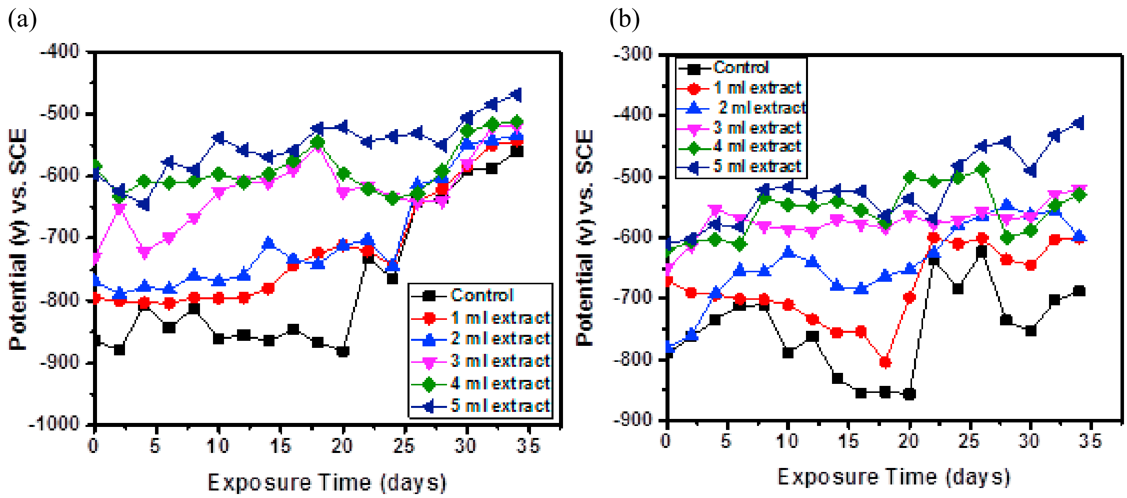

Figure 4: Variation of corrosion potential with exposure time for heat-treated mild steel in the presence of 1-5 ml lecaniodiscus cupaniodes extract for (a) annealed and (b) normalized mild steels.

Most negative potentials were obtained for the tests carried out without the plant extract (control). This result compares well with literature on inhibition effects on corrosion potential [11]. The more negative corrosion potential indicates active corrosion reactions while the more positive potential suggests passive corrosion reactions. The potential increases with increase in inhibitor concentration and the most positive value (-412 volts on the 34th day of exposure) was obtained for normalized mild steel with 5 ml inhibitor which is also the best corrosion inhibition concentration for the entire experiment.

Conclusion

The effect of *lecaniodiscus cupaniodes* in the corrosion inhibition of annealed and normalized mild steels in 0.5 M HCl have been investigated. The inhibitive effect of the extract relapsed with increase in exposure time for annealed mild steel in 0.5 M HCl. Corrosion resistance of normalized mild steel was generally higher than that of the annealed mild steel both in the presence and absence of the inhibiting agent. Corrosion rates of the two heat-treated steels were significantly affected by the concentration of *lecaniodiscus cupaniodes* extract. In general, *Lecaniodiscus cupaniodes* performed effectively at inhibiting the rate of corrosion attack on the heat-treated steels in 0.5 M HCl medium with an average inhibition efficiency of 90 percent (%).

Acknowledgements

The Department of Mechanical Engineering, Covenant University, Ota, Nigeria is acknowledged for the provision of research facilities for this work. Covenant University is also acknowledged for providing funds to publish in open access.

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